On the value of the Curie temperature in doped manganites

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We have verified that the variational mean field theory approach suggested by Narimanov and Varma (preprint cond-mat/0002191) being applied to the realistic two-band model provides a good agreement with experimental data for the Curie temperature in doped manganites $A_{1-x}B_x MnO_3$ ($x \simeq 0.3$). We have also considered the problem of an interplay between the ferromagnetic and antiferromagnetic interactions by using the same approach.

The problem of finding the value of the critical temperature for the paramagnetic-to-ferromagnetic transition in doped manganites has presented a lot of interest recently. An agreement of theoretical predictions with experimental results for the Curie temperature may shed some light on physical mechanisms driving the transition near the concentration region, where the colossal magneto-resistance (CMR) effect takes place.

An interesting approach for obtaining the value for the transition temperature has been recently proposed by Narimanov and Varma[1] (see also[2]) and is based on the variational mean field theory within the formalism of the double exchange (DE) model[3-5]. The final result for the critical temperature dependence on concentration[1,2] can be approximately written in the following form:

$$T_c \simeq x\,(1-x)\,W, \tag{1}$$

where W is a bandwidth. For $W = 1.8$ eV and $0.15 \le x \le 0.3$ Eq. (1) recovers the experimentally observed values for the Curie temperature. This result can be generalized in such a way, that the DE model works well in order to describe the physics near the CMR region[6,7] and in principle one does not need to take into account other mechanisms[8,9] which might effect the transition.

In what follows we adopt the variational mean field theory scheme for the DE model via degenerate orbitals[10] in order to verify the validity of the two-band approach[11,12] near the CMR region. In the DE model within the two-band scheme, there is no electron-hole symmetry, which means that the Curie temperature is non-symmetric with respect to substitution $x \to 1 - x$. Since for the small concentrations percolation effects play an essential role[11,13], we will be primarily concerned with obtaining the value for the Curie temperature near the CMR region ($x \sim 0.3$). As we will see, the approach we are using works well and recovers the right numerical value for the Curie temperature in units of hopping amplitude the value for which in the two-band model for manganites has been estimated in[12]. The relative simplicity of present approach also allows us to consider a problem of suppression of the ferromagnetic transition by the superexchange interaction[14-16].

We consider three t_{2g} electrons on a Mn ion as the localized classical spins. The Hamiltonian for the DE model on the degenerate orbitals can be defined as:

$$H_{DE} = -\sum_{\langle ij \rangle} t_{ij}^{ab} \cdot c_{ia\alpha}^{\dagger} c_{jb\alpha} \; - \; J_H \sum_{i} \vec{S}_i \cdot c_{ia\alpha}^{\dagger} \vec{\sigma}_{\alpha\beta} c_{ia\beta}. \tag{2}$$

The matrix elements t_{ij}^{ab} describe the electrons, hopping from one site to another, on two-fold degenerate e_g orbitals. As it was shown by Anderson and Hasegawa [4], in the limit of strong Hund's coupling, the hopping amplitude of the electrons between the sites i and j acquires an angular dependence $t_{ij} = t(\theta_{ij})$, where θ_{ij} is the angle between the core spins $\vec{S}_i$ and $\vec{S}_j$. In the DE model the hopping amplitude is the largest, when the spins are aligned, which means that a ferromagnetic state minimizes the kinetic energy. Thus, the effective Hamiltonian for our problem can be written as:

$$H = H_{DE} + J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j. \tag{3}$$

We employ the variational mean field theory by introducing the spin orientation distribution function $P(\Omega) = \frac{1}{2\pi} P(\vartheta)$. In the mean field approximation, the distribution function depends only on single spin orientation, which is described by an angle ϑ. The idea is to represent the free energy of our system as a functional of $P(\vartheta)$ and, following the standard mean field treatment, to find the self-consistent equation for the distribution function.

The free energy is defined as:

$$F = E_{el} + E_{spin} - T \cdot S_{spin}, \tag{4}$$

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where S_{spin} is the entropy of our system, E_{el} is electron energy, E_{spin} is the spin energy.

As mentioned above, the distribution function for the system of spins is just the product of the distribution functions of the individual spins. Thus, in the semiclassical limit, the entropy can be written as:

$$S_{spin} = -\int\limits_0^\pi d\vartheta \sin \vartheta P(\vartheta) \log[P(\vartheta)]. \tag{5}$$

In the absence of a magnetic field, the spin energy contribution, E_{spin}, in the classical limit, is just the average of the superexchange Hamiltonian:

$$E_{spin} = \frac{J}{2} \int\limits_0^{2\pi} \frac{d\phi_1}{2\pi} \int\limits_0^{2\pi} \frac{d\phi_2}{2\pi} \int\limits_0^\pi d\vartheta_1 \sin \vartheta_1 P(\vartheta_1) \int\limits_0^\pi d\vartheta_2 \sin \vartheta_2 P(\vartheta_2) \cos(\theta), \tag{6}$$

where $\cos(\theta) = \cos \vartheta_1 \cos \vartheta_2 + \sin \vartheta_1 \sin \vartheta_2 \cos(\phi_1 - \phi_2)$.

The electron energy is calculated as follows. First, we calculate the energy for a given spin distribution, $E[t]$ and then we just take the average of $E[t]$ over all possible spin configurations:

$$E_{el} = \int dt P(t) E[t]. \tag{7}$$

To calculate $E[t]$ we adopt the tight binding approximation. For the two-dimensional representation e_g we choose the normalized complex functions ψ_1 and ψ_2, given by[11]:

$$\psi_1 \propto z^2 + \epsilon x^2 + \epsilon^2 y^2, \ \psi_2 \equiv \psi_1^*, \tag{8}$$

where $\epsilon = \exp(2\pi i/3)$.

The cubic spectrum consists of two branches:

$$\varepsilon_{1,2}(\mathbf{p}) = -t(\theta) \cdot \left\{ (c_x + c_y + c_z) \pm \sqrt{c_x^2 + c_y^2 + c_z^2 - c_x c_y - c_y c_z - c_z c_x} \right\} \tag{9}$$

(we introduced the notations $c_i = \cos(k_i a), i = x, y, z$). Since there is an interaction between the e_g electrons and the magnetic background, following the discussion by Anderson and Hasegawa, we have introduced the effective hopping amplitude $t(\theta) = |A| \cos(\theta/2)$ (θ is the angle between the two neighboring spins and $|A|$ is a hopping amplitude, whose numerical value will be defined later).

Thus, the electron energy for a given spin configuration is:

$$E[t] = \sum_{i=1}^2 \int \frac{d\mathbf{k}}{(2\pi)^3} \varepsilon_i(\mathbf{k}, \theta) \cdot n_F[\varepsilon_i(\mathbf{k}, \theta)], \tag{10}$$

where n_F is Fermi distribution function.

Using the expressions (5,6,10) and the Lagrange variational method, the free energy functional acquires the following form:

$$F[P_\vartheta; \mu, \xi] = \int\limits_0^{2\pi} \frac{d\phi_1}{2\pi} \int\limits_0^{2\pi} \frac{d\phi_2}{2\pi} \int\limits_0^\pi d\vartheta_1 \sin \vartheta_1 P(\vartheta_1) \int\limits_0^\pi d\vartheta_2 \sin \vartheta_2 P(\vartheta_2) \times$$

$$\left\{ \sum_{i=1}^2 \int \frac{d\mathbf{k}}{(2\pi)^3} (\varepsilon_i(\mathbf{k}, \theta) - \lambda) \times n_F[\varepsilon_i(\mathbf{k}, \theta)] + \frac{J}{2} \cos(\theta) \right\} + T \int\limits_0^\pi d\vartheta \sin \vartheta \times$$

$$P(\vartheta) \log[P(\vartheta)] + \xi \int\limits_0^\pi d\vartheta \sin \vartheta P(\vartheta) - \mu_B SB \int\limits_0^{2\pi} \frac{d\phi_1}{2\pi} \int\limits_0^\pi d\vartheta_1 \times$$

$$\sin \vartheta_1 \cos \vartheta_1 P(\vartheta_1) + \widetilde{F}[\lambda, \xi] \tag{11}$$

(λ is a Lagrange multiplier, being a constraint to have a constant number of conduction electrons in our system, ξ is a Lagrange multiplier, which provides the normalization for $P(\vartheta)$ and $\widetilde{F}[\lambda, \xi]$ is a ϑ independent part of the free

energy, B is a external magnetic field). Since the number of conduction electrons is conserved in our system, the free energy functional acquires its minimal value for λ being equal to the chemical potential μ, which is defined, in our case, by the following expression:

$$1 - x = \sum_{i=1}^{2} \int \frac{d\mathbf{k}}{(2\pi)^3} n_F[(\varepsilon_i(\mathbf{k}, \theta = 0) - \mu)/T],$$

where x is the hole concentration.

Now, taking the functional derivative of (11) with respect to $P(\vartheta)$, we obtain the following integral equation:

$$P(\vartheta) = \exp\left[-2 \int_0^{2\pi} \frac{d\phi_1}{2\pi} \int_0^{2\pi} \frac{d\phi_2}{2\pi} \int_0^{\pi} d\vartheta_1 \sin\vartheta_1 P(\vartheta_1) \times \right.$$

$$\left\{ \sum_{i=1}^{2} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{(\varepsilon_i(\mathbf{k}, \theta) - \mu)}{T} n_F[\varepsilon_i(\mathbf{k}, \theta)] + \frac{J}{2T} \cos(\theta) \right\} -$$

$$\left. \xi/T + \frac{\mu_B S B}{T} \cos\vartheta \right]. \tag{12}$$

The integral equation (12) is nothing but *variational* mean-field theory equation for the distribution function $P(\vartheta)$, where $P(\vartheta)$ plays the role of the order parameter. If the system is in the paramagnetic phase, $P(\vartheta)$ is uniform. Equation (12) allows a numerical solution. Its results are shown on Fig. 1.
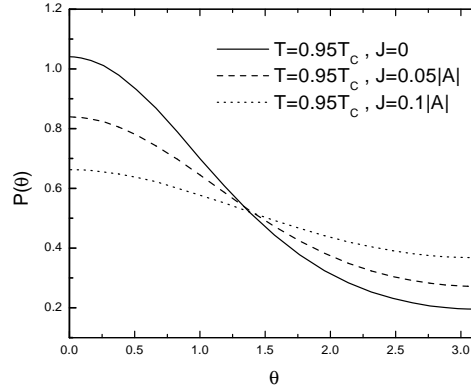

FIG. 1. The single spin orientation distribution function $P(\vartheta)$ is shown as a function of ϑ for different values of the antiferromagnetic exchange constant J. The results are obtained for hole concentration $x \simeq 0.3$.

As soon as the temperature decreases (in the presence of a small magnetic field) and approaches the Curie temperature T_c, small deviations from the uniform distribution will appear in $P(\vartheta)$:

$$P(\vartheta)|_{T \to T_c} = \frac{1}{2} + \Delta(\vartheta), \quad \Delta(\vartheta) \ll 1. \tag{13}$$

Since $\Delta(\vartheta)$ is small, we can expand both sides of Eq. (12) in powers of $\Delta(\vartheta)$, keeping only the linear terms and solving the final expression for $\Delta(\vartheta)$. The results can be written in the following form:

$$\Delta(\vartheta) \propto \frac{B \cos\vartheta}{T - T_c},$$

$$T_c = \int_0^{\pi} d\vartheta \, \sin\vartheta \, \cos\vartheta \left\{ \sum_{i=1}^{2} \int \frac{d\mathbf{k}}{(2\pi)^3} (\mu - \varepsilon_i(\mathbf{k})) \times n_F[\varepsilon_i(\mathbf{k})] - \frac{J}{2} \cos(\vartheta) \right\}. \tag{14}$$

Thus, as it is seen from (14), the ferromagnetic transition is linearly suppressed by the superexchange interaction, in agreement with previous results obtained in[14]. The energy scale is defined in the units of the hopping amplitude,

| A |. The experimental results for the spin-wave stiffness coefficient provide | A |=0.16 eV (see e.g.[12] and references therein).

As we see in Fig. 2, T_c decreases as system is doped with holes. For concentrations, where the CMR effect is very pronounced ($x \simeq 0.3$), the value we found for the critical temperature is equal to 390 K, which is in good agreement with the experimental data. Hence, the DE model via degenerate orbitals alone gives a good value for the critical temperature. For small concentrations our result does not agree with experimental observations, in which T_c is increasing with doping. Such a behavior for small concentrations can be explained in terms of percolation theory (see[11−13] and references therein) and can not be captured by using the present approach.
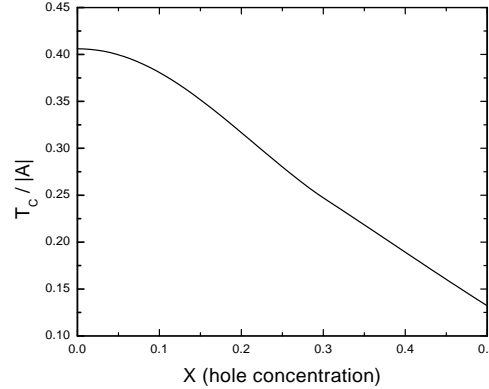

FIG. 2. Curie temperature is plotted as a function of hole concentration x.

In conclusion, we have shown, that the variational mean field theory can successfully describe the paramagnetic-to-ferromagnetic transition for $x \sim 0.3$ in the frame of the DE model when the two-fold degeneracy of the e_g levels is taken into account. We have also discussed the competition between the ferromagnetic and antiferromagnetic exchange interactions. Although the phonons might play an essential role in the high-temperature properties of the manganites near the metallic region (isotope effect), the other mechanism for suppressing the ferromagnetic phase is the superexchange interaction between the t_{2g} core spins.

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